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(71) Applicant: **CIBA-GEIGY AG**  
**Klybeckstrasse 141**  
**CH-4002 Basel (CH)**

(72) Inventor: **Capocci, Gerald A.**  
**25 Greenway Drive**  
**Greenwich, CT 06431 (US)**

**Zappla, Jean M.**  
**3 Hollywood Street**  
**Mohegan Lake, NY 10547 (US)**

(54) **Stabilization systems for polyacetals.**

(57) **A blend of a phenolic antioxidant and a hydrazine or oxamido derivative in appropriate proportions for use in stabilizing acetal homo- and copolymers against oxidative and thermal degradation.**

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The instant invention pertains to an acetal homo- or copolymer composition comprising a hindered phenol and a specific hydrazine compound or oxamido compound, to a method of stabilizing acetal homo- or copolymers as well as to a method of reducing color formation in acetal homo- or copolymers which contain a hindered phenol.

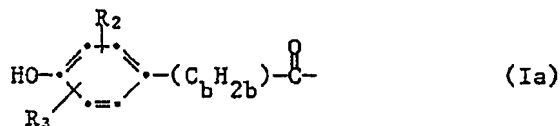
Polycetal homo- and copolymers are well known to those skilled in the art. These materials are a suitable replacement for metal in numerous applications as a result of properties such as high strength and stiffness, good fatigue life, excellent resilience and toughness, low moisture sensitivity, solvent resistance, excellent electrical characteristics and the capability to maintain these properties at elevated temperatures. The molecular structure of the polymer is that of a linear acetal, consisting of unbranched polyoxymethylene chains of substantial length, generally averaging more than 1000  $-CH_2O-$  units. The acetal homopolymers are, for example, prepared by the polymerization of anhydrous formaldehyde or by the polymerization of trioxane. Acetal copolymers are typified, for example, by the polymerization product of trioxane and a cyclic ether such as ethylene oxide.

Since polyacetals are subject to oxidative and thermal degradation and discoloration, a wide variety of light stabilizers and antioxidants have been recommended for use therein. Included among the latter are diverse hindered phenolic antioxidants as reflected for example in U.S. Patents 3,285,855, 3,644,482 and the like; as well as various hydrazine compounds as reflected for example in U.S. Patents 3,110,696 and 3,660,438. Although these groups of compounds have provided antioxidant properties to polyacetals, levels of discoloration during storage and exposure particularly with the hindered phenols have proven to be unacceptably high for certain end uses. This potential deficiency is aggravated by the fact that the hindered phenol primary stabilizers are required in order to provide maximum thermal stability, the latter not being provided by the individual use of co-stabilizers even at higher concentration levels.

It has now been discovered that by including a special hydrazine or oxamido compound with a special hindered phenol in the proportions noted hereinafter as a stabilizing system for acetal homo- and copolymers, total stabilizing activity is achieved. Thus, the blend provides excellent stabilization against both oxidative and thermal degradation. Of primary importance, the combination provides significantly improved performance in the area where the individual hindered phenol is lacking, namely, in resistance to discoloration during storage and/or exposure to environmental conditions. In fact, contrary to expectation, the use of higher levels of hindered phenol in such combinations does not result in a concomitant increase in discoloration of the acetal polymer.

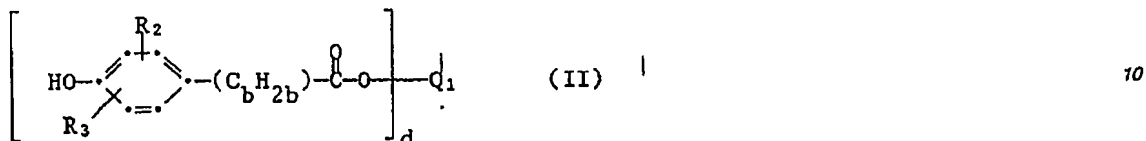
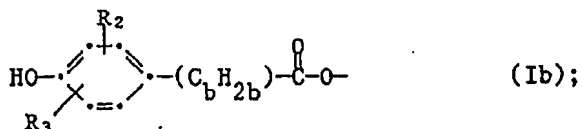
As previously noted, the applicable hindered phenols and hydrazine or oxamido compounds are known to those skilled in the art and have been identified as antioxidants for use in acetal polymers. Various blends of the hindered phenol and hydrazine components have been identified for use as stabilizer systems for polyolefins, polyurethans and various elastomers. In addition, U.S. Patent 3,940,365 describes moulding compositions based on poly(oxymethylene) which contain a phenolic antioxidant and a specific compound having a nucleating effect. However, the unexpected performance pattern achieved with the use of the instant blends clearly provide a distinct situation.

The instant invention pertains to an acetal homo- or copolymer which comprises (a) a hindered phenol corresponding to the formula I, II, III, IV, V, VI or VII,  $R_1X-(C_6H_2a)-Q$  (I) wherein  $R_1$  is a group of the formula Ia.

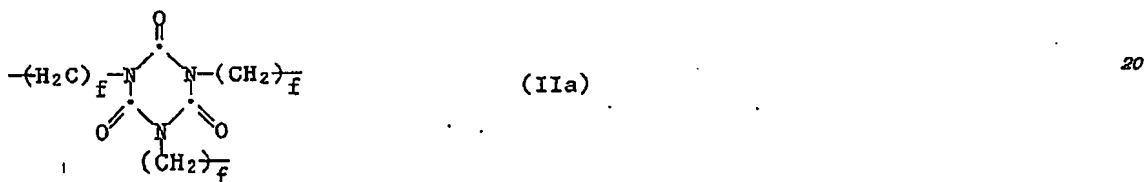


X is oxygen or sulfur, a is an integer from 6 to 30, preferably 6 to 18, b is an integer from 0 to 6, R<sub>2</sub> and R<sub>3</sub> are independently C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, phenyl or C<sub>7</sub>-C<sub>9</sub>aralkyl, and R<sub>2</sub> is also hydrogen, Q is hydrogen or -A-(C<sub>2</sub>H<sub>5</sub>)-R<sub>4</sub>, A is oxygen, sulfur or -N-,

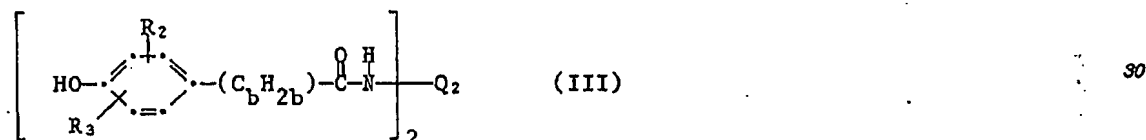
y is an Integer from 2 to 20,  
B is C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkanoyl, and R<sub>4</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkanoyloxy or a group of the formula Ib.



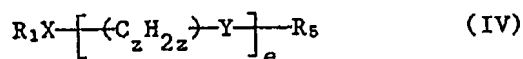
wherein R<sub>2</sub>, R<sub>3</sub> and b are as defined above, d is an integer from 2 to 6, and Q<sub>1</sub> is a d-valent aliphatic hydrocarbon of 1 to 18 carbon atoms, a d-valent aromatic or aromatic aliphatic hydrocarbon of 6 to 20 carbon atoms or a group of the formula IIa



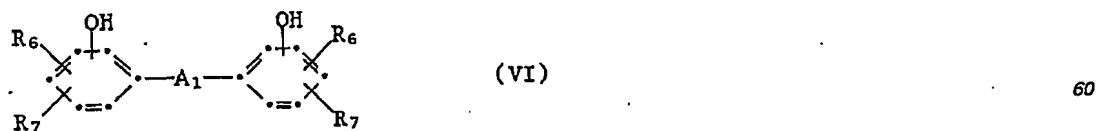
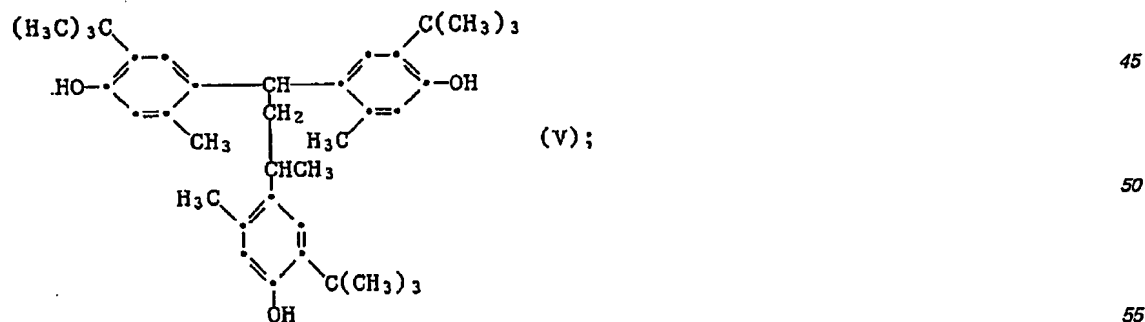
wherein f is an integer from 1 to 4;



wherein R<sub>2</sub>, R<sub>3</sub> and b are as defined above, and Q<sub>2</sub> is C<sub>1</sub>-C<sub>18</sub>alkylene;



wherein R<sub>1</sub> and X are as defined above, z is an integer from 2 to 6, e is an integer from 3 to 40, preferably 3 to 10, Y is oxygen or sulfur, and R<sub>5</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or a group of the formula Ia;

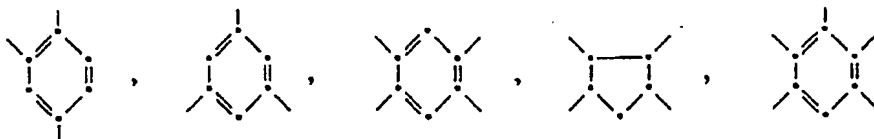


wherein R<sub>6</sub> and R<sub>7</sub> are independently C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, phenyl or C<sub>7</sub>-C<sub>9</sub>aralkyl, and R<sub>8</sub> is also hydrogen, and A<sub>1</sub> is a group  $\text{>C(R}_8\text{)}_2$ , wherein R<sub>8</sub> and R<sub>9</sub> are independently hydrogen or C<sub>1</sub>-C<sub>8</sub>alkyl;



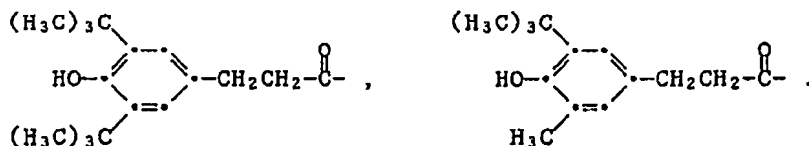
phenylene, phenylene substituted by one or more C<sub>1</sub>-C<sub>4</sub>alkyl, or naphthylene.

Q<sub>1</sub> as a trivalent, tetravalent or pentavalent hydrocarbon can be e.g. a group of the following formulae

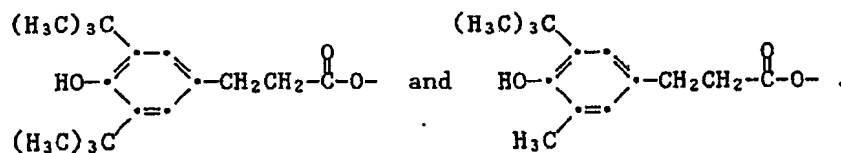


or alkanetriyl of 3 to 6 carbon atoms, such as e.g. glyceryl or trimethylpropyl or alkanetetrayl of 4 to 6 carbon atoms such as e.g. pentaerythrityl.

Formula Ia represents preferably one of the following groups:



Formula Ib is in particular one of the groups



In the group of the formula IIa f is preferably 2.

Those compositions are preferred, wherein component (a) is a compound of the formula I, II, III, IV, V or VI, in particular I, II, III or IV.

Z is preferably a direct bond or C<sub>1</sub>-C<sub>8</sub>alkylene.

Compounds of formula I which are preferred exhibit X as oxygen, b as an integer from 0 to 2, R<sub>2</sub> and R<sub>3</sub> as alkyl of 1 to 8 carbon atoms, A as oxygen, y as 2, R<sub>4</sub> as hydrogen or a group of the formula Ib. Particularly preferred are those compounds wherein R<sub>2</sub> and R<sub>3</sub> are tert-butyl positioned ortho to the hydroxyl group and b is 2. A specific compound of preference is octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate.

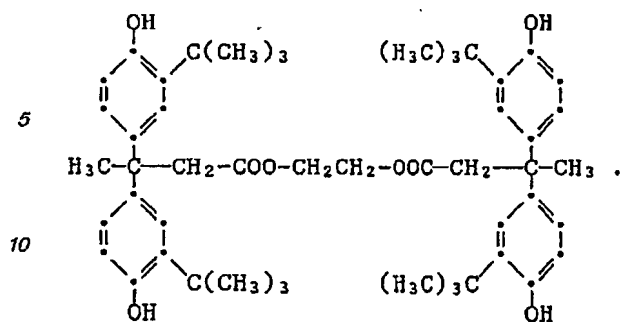
Compounds of formula II which are preferred exhibit R<sub>2</sub> and R<sub>3</sub> as C<sub>1</sub>-C<sub>8</sub>alkyl, in particular tert-butyl positioned ortho to the hydroxyl group, b as 2, d as 2 or 4 and Q<sub>1</sub> as C<sub>2</sub>-C<sub>10</sub>alkylene or pentaerythrityl. Specific compounds of preference are 1,6-hexamethylene bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] and tetrakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane.

Compounds of formula III which are preferred exhibit R<sub>2</sub> and R<sub>3</sub> as C<sub>1</sub>-C<sub>8</sub>alkyl and preferably tert-butyl positioned ortho to the hydroxyl group, b as 2 and Q<sub>2</sub> as C<sub>2</sub>-C<sub>8</sub>alkylene. The specific compound of preference is N,N'-hexamethylene bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

Compounds of formula IV which are preferred exhibit X and Y as oxygen, b as an integer from 0 to 2, R<sub>2</sub> and R<sub>3</sub> as alkyl of 1 to 8 carbon atoms, z as 2, e as an integer from 3 to 20, and R<sub>5</sub> as a group of the formula Ia. Particularly preferred are those compounds wherein R<sub>2</sub> and R<sub>3</sub> are tert-butyl positioned ortho to the hydroxyl group. A specific compound of preference is triethylene glycol bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

Compounds of formula VI which are preferred exhibit R<sub>6</sub> and R<sub>7</sub> as methyl or tert-butyl and R<sub>8</sub> and R<sub>9</sub> as hydrogen or methyl. Specific compounds of preference are bis[2-hydroxy-3-tert-butyl-5-methylphenyl]methane and 1,1-bis[2'-hydroxy-3',5'-di-tert-butylphenyl]ethane.

A preferred compound of formula VII is



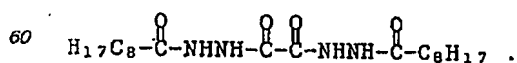
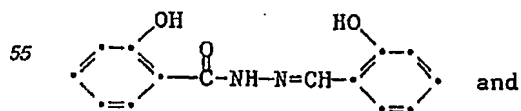
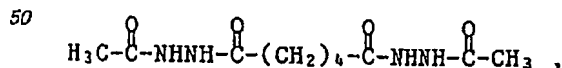
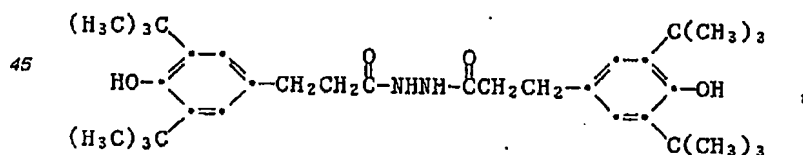
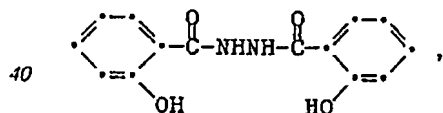
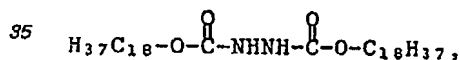
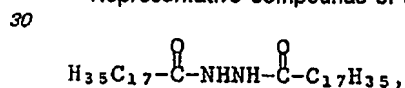
15 Preferred compositions of the invention are those wherein component (a) is octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, 1,6-hexamethylene bis[3-(3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate), tetrakis-[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamamide] or triethylene glycol bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

20 According to a further preferred embodiment in component (b) R<sub>12</sub> and R<sub>13</sub> are independently C<sub>1</sub>-C<sub>18</sub>alkyl or a group of formula VIIIa, Z is a direct bond or C<sub>1</sub>-C<sub>6</sub>alkylene and the radicals R<sub>14</sub> are independently C<sub>4</sub>-C<sub>8</sub>alkyl, C<sub>5</sub>-C<sub>8</sub>cycloalkyl, phenyl or benzyl.

25 Preferred groups of the formula VIIIa and preferred compounds of the formula X are those wherein the OH group is either in the ortho- or para-position. When the OH group is in the para-position, the groups of the formula VIIIa preferably contain two R<sub>14</sub> radicals positioned ortho to the hydroxyl group, which are alkyl of 4 to 8 carbon atoms and most preferably tert-butyl.

With respect to compounds of formula X, the OH group is preferably in the ortho-position to the linking chain.

Representative compounds of component (b) include



Another preferred composition of the instant invention contains as component (a) 1,6-hexamethylene bis[3-(3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate)] and as component (b) N,N'-bis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine. The combination of these components particularly reveals a performance

improvement in the hindered phenol.

Preferred compositions are also those which contain components (a) and (c).

In compounds of the formula XI R<sub>15</sub> is preferably a group of the formula VIIIa with the OH radical in the para-position and two R<sub>14</sub> groups positioned ortho to the hydroxyl group, R<sub>14</sub> being preferably tert-butyl. A representative compound is 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] (®NAUGARD XL-1 from Unlroyal).

Methods for preparing the compounds of component (a) are well known to those skilled in the art. Specific reference is made to U.S. Pat. Nos. 3,285,855, 3,531,483, 3,584,047, 3,632,553, 3,644,482, 3,944,594, 4,032,562 and 4,507,420 for information regarding the phenols of formula I-IV and VI and their methods of preparation. The compound of formula V is ®TOPANOL CA available from ICI Corp. The compounds of formula VII can be prepared as described, for example, in U.S. Patent 3,960,928.

The compounds of component (b) and methods for their preparation are disclosed in U.S. Pat. Nos. 3,110,696 and 3,660,438, said disclosures being fully incorporated herein.

In general, the blends of the present invention are employed in from about 0.01 to about 10 % by weight of the stabilized composition, although this will vary with the particular application. An advantageous range is from about 0.05 to about 2 %, and especially 0.1 to about 1 %. The weight ratio of component (a) to component (b) or component (c) will generally range from 20:1 to 1:10, preferably 9:1 to 1:9, and most preferably 2-3:1.

The stabilizers of the instant invention, either individually or in combination, may readily be incorporated into the acetal polymers by conventional techniques, at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizers may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension, or emulsion of the polymer. The resulting stabilized polymer compositions of the invention may optionally also contain various conventional additives. Included among these additives are basic co-stabilizers such as calcium citrate, melamine, cyanoguanidine, polyamides, alkali and alkaline earth metal salts of high fatty acids, and amines; phosphites and phosphonites; peroxide-destroying compounds such as esters of thiodipropionic acid; and the like.

The instant invention also relates to a method of stabilizing an acetal homo- or copolymer against thermal or oxidative degradation, which comprises incorporating into said acetal components (a) and (b) or (a) and (c) as defined above.

Another embodiment of the instant invention is a method of reducing color formation in acetal homo- or copolymers containing a hindered phenol (component (a)), which comprises incorporating into said acetal homo- or copolymers component (b) or (c) as defined above.

The following examples illustrate the embodiments of this invention.

#### Test compounds

- A - 1,6-hexamethylene bis[3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate]
- B - triethylene glycol bis[3-tert-butyl-5-methyl-4-hydroxyphenyl]propionate
- C - tetrakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane
- D - N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamamide]
- E - octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate
- F - 1,3,5-tris[3',5'-di-tert-butyl-4'-hydroxybenzoyloxyethyl]isocyanurate
- G - 1,1,3-tris[3'-tert-butyl-4'-hydroxy-5'-methylphenyl]butane
- H - 1,1-bis[3'-tert-butyl-4'-hydroxy-5'-methylphenyl]butane
- J - N,N'-bis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)proplonyl]hydrazine
- K - 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]

#### Example 1:

The additives in the indicated concentrations are dry blended into polyoxymethylene resin (trioxane-ethylene oxide copolymer (®CELCON from Celanase) with base stabilization system of 0.2 % bis-stearamide and 0.1 % calcium hydroxystearate] and extruder compounded (single extrusion) into pellets at 185°C. The pellets are stored in a dark area in glass petri dishes at ambient temperatures for the indicated time periods and specimen yellowness index (YI) is determined according to ASTM D 1925.

Components	Conc. (% by wt.)	Yellowness Index		
		Initial	64 Days	131 Days
A	0.5	3.6	10.4	11.3
J	0.5	3.6	2.7	2.3
A/J	0.25/0.25	2.0	1.5	1.3
A/J	0.3/0.2	1.5	1.2	1.2
A/J	0.35/0.15	2.3	2.0	1.8
A/J	0.4/0.1	1.9	1.5	1.4
A/J	0.45/0.05	1.4	1.2	1.5
A/J	0.475/0.025	1.2	1.0	1.0
A/J	0.2/0.3	1.0	1.4	1.3
A/J	0.15/0.35	2.6	1.8	1.6
A/J	0.1/0.4	2.7	2.1	2.0
A/J	0.05/0.45	2.2	1.7	1.6
K	0.5	1.7	1.7	2.0
A/K	0.25/0.25	1.0	1.9	2.1
A/K	0.35/0.15	1.4	2.8	3.2
A/K	0.45/0.05	1.7	3.0	3.4
A/K	0.15/0.35	1.6	2.3	2.6
A/K	0.05/0.45	1.4	2.0	2.4

These data thus indicate the high resistance to discoloration during dark storage as exhibited by the stabilized systems of this invention. In addition, significant performance improvement is exhibited relative to component A, the more highly discoloration antioxidant.

#### Example II:

The procedures of Example I are repeated with the exception of certain of the components of the base acetal and the aging conditions. Thus, the formulated systems are subjected to oven aging at 80°C and to storage in water at 70°C.



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<u>COSTA- BILIZER 0.3 % Ca STEARATE</u>	<u>Oven aging at 80° C <math>\Delta</math>YI at 20 Weeks</u>	<u>Storage in Water at 70° C YI at 20 Weeks</u>	
0.3 % A	18.7	33.4	5
0.3 % A + 0.01 % J	13.1	17.3	
0.3 % A + 0.03 % J	12.0	14.7	
0.3 % A + 0.05 % J	12.8	13.0	10
<u>COSTA- BILIZER 0.15 % Ca CITRATE</u>			15
0.3 % A	18.0	10.2	
0.3 % A + 0.01 % J	13.1	8.3	
0.3 % A + 0.03 % J	14.5	8.6	20
0.3 % A + 0.05 % J	12.5	8.2	
<u>COSTA- BILIZER 0.3 % MELAMINE</u>			25
0.3 % A	10.6	9.8	
0.3 % A + 0.01 % J	9.0	7.5	
0.3 % A + 0.03 % J	8.1	9.0	30
0.3 % A + 0.05 % J	8.1	8.3	
<u>COSTA- BILIZER 0.3 % CYANOQUA- NIDINE</u>			35
0.3 % A	10.5	16.4	
0.3 % A + 0.01 % J	9.0	7.2	
0.3 % A + 0.03 % J	10.2	7.3	
0.3 % A + 0.05 % J	10.1	6.0	45

Example III:

Example I is repeated utilizing a variety of phenolic antioxidants.

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	Additive	Conc. (% by wt.)	YI Initial	YI 45 Days
	A	0.5	4.0	16.2
5	A/J	0.4/0.1	4.1	5.0
	B	0.5	3.8	4.0
	B/J	0.4/0.1	2.2	2.8
	C	0.5	3.8	13.0
	C/J	0.4/0.1	2.5	4.0
10	D	0.5	3.0	8.0
	D/J	0.4/0.1	3.0	4.1
	E	0.5	4.1	26.6
	E/J	0.4/0.1	5.5	7.2
15	F	0.5	9.2	14.5
	F/J	0.4/0.1	8.5	11.1
	G	0.5	11.1	14.9
	G/J	0.4/0.1	5.4	7.2
	H	0.5	12.0	21.8
20	H/J	0.4/0.1	5.6	7.0
	J	0.5	4.1	5.3

#### 25 Example IV:

Example III is repeated with the exception that the resulting samples are subjected to oven aging for five days at 110°C.

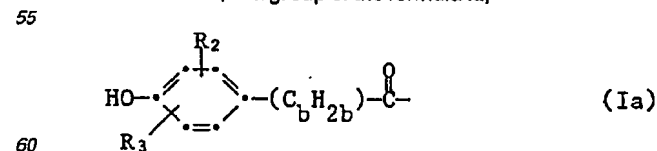
	Additive	Conc. (% by wt.)	YI - Oven Aged
30	C	0.5	23.3
	C/J	0.475/0.025	17.7
	E	0.5	23.2
35	E/J	0.475/0.025	13.3
	F	0.5	39.7
	F/J	0.475/0.025	25.9
	J	0.5	28.3

40 It is thus seen that the instant combination of antioxidants provides significantly improved stabilization effectiveness in acetal polymers. This improvement is particularly evident in a key indicia of stabilization, namely, resistance to discoloration.

45 In summary, this invention provides antioxidant systems for stabilizing acetal polymers against oxidative and thermal degradation. Variations may be made in various elements thereof without departing from the scope of the invention as defined by the following claims.

#### Claims

- 50 1. An acetal homo- or copolymer which comprises  
 (a) a hindered phenol corresponding to the formula I, II, III, IV, V, VI or VII,  
 $R_1X-(C_6H_2a)-Q$  (I)  
 wherein  $R_1$  is a group of the formula Ia,

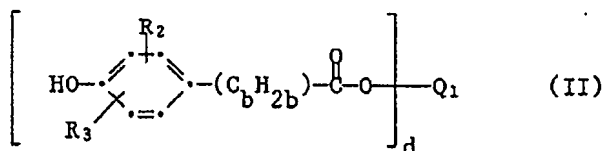
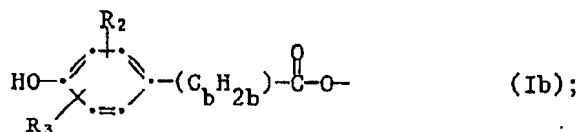


X is oxygen or sulfur, a is an integer from 6 to 30, b is an integer from 0 to 6,  $R_2$  and  $R_3$  are independently  $C_1$ - $C_{18}$ alkyl,  $C_5$ - $C_{12}$ cycloalkyl, phenyl or  $C_7$ - $C_9$ aralkyl, and  $R_2$  is also hydrogen, Q is hydrogen or  $-A(C_7H_{27})-R_4$ , A is oxygen, sulfur or  $-N-$ ,

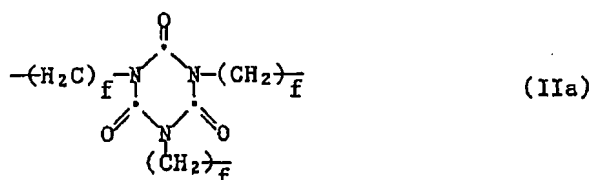
65  $B$

**y is an integer from 2 to 20,**

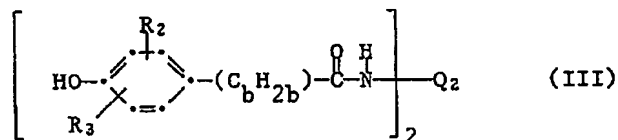
B is C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkanoyl, and R<sub>4</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkanoyloxy or a group of the formula Ib,



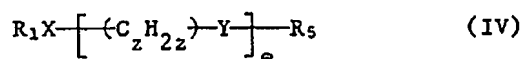
wherein R<sub>2</sub>, R<sub>3</sub> and b are as defined above, d is an integer from 2 to 6, and Q<sub>1</sub> is a d-valent aliphatic hydrocarbon of 1 to 18 carbon atoms, a d-valent aromatic or aromatic aliphatic hydrocarbon of 6 to 20 carbon atoms or a group of the formula IIa



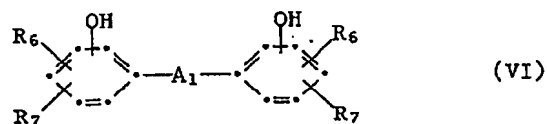
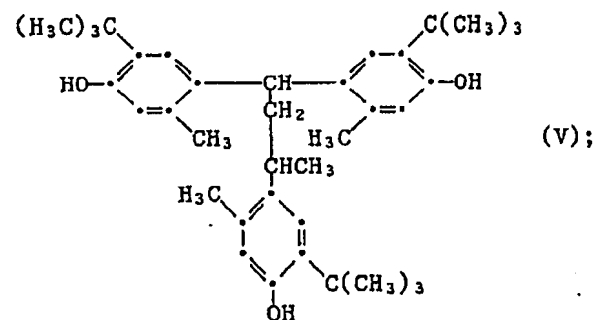
wherein  $f$  is an integer from 1 to 4;



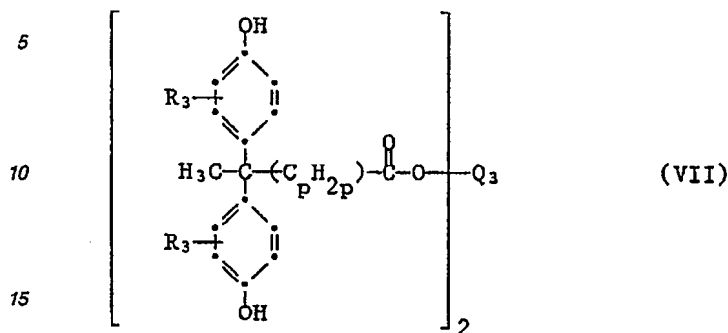
wherein R<sub>2</sub>, R<sub>3</sub> and b are as defined above, and Q<sub>2</sub> is C<sub>1</sub>-C<sub>18</sub>alkylene;



wherein R<sub>1</sub> and X are as defined above, z is an integer from 2 to 6, e is an integer from 3 to 40, Y is oxygen or sulfur, and R<sub>5</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or a group of the formula Ia;



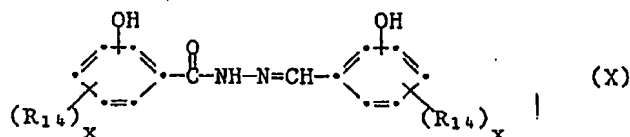
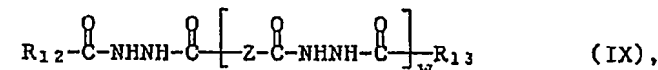
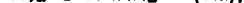
wherein  $R_6$  and  $R_7$  are independently  $C_1$ - $C_{18}$ alkyl,  $C_5$ - $C_{12}$ cycloalkyl, phenyl or  $C_7$ - $C_9$ aralkyl, and  $R_8$  is also hydrogen, and  $A_1$  is a group  $\text{>C}(R_8)R_9$ , wherein  $R_8$  and  $R_9$  are independently hydrogen or  $C_1$ - $C_8$ alkyl;



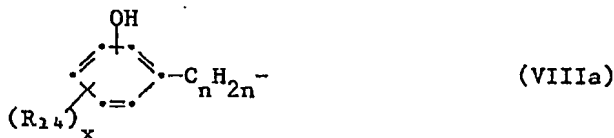
wherein  $R_3$  is as defined above,  $p$  is 1 or 2 and  $Q_3$  is  $C_2$ - $C_{10}$ alkylene;

and

(b) a hydrazine compound corresponding to the formula VIII, IX or X

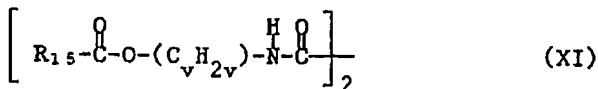


wherein  $R_{12}$  and  $R_{13}$  are independently  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyloxy, phenyl,  $C_7$ - $C_9$ aralkyl or a group of the formula VIIIa,



$Z$  is a direct bond,  $C_1$ - $C_{18}$ alkylene or phenylene, the radicals  $R_{14}$  are independently  $C_1$ - $C_{18}$ alkyl,  $C_5$ - $C_{12}$ cycloalkyl, phenyl or  $C_7$ - $C_9$ aralkyl,  $w$  is 0 or 1,  $x$  is an integer from 0 to 4 and  $n$  is an integer from 0 to 6, with the proviso that  $x$  is different from zero, when  $w$  is 1; or

(c) an oxamido compound of the formula XI



wherein  $R_{15}$  is  $C_1$ - $C_{18}$ alkyl, phenyl,  $C_7$ - $C_9$ aralkyl or a group of the formula VIIIa and  $v$  is an integer from 0 to 6; the weight ratio of the components (a):(b) or (a):(c) is 20:1 to 1:10.

2. The composition of claim 1, wherein said hindered phenol corresponds to the formula I, II, III, IV, V or VI.

3. The composition of claim 1, wherein said hindered phenol corresponds to formula I.

4. The composition of claim 1, wherein said hindered phenol corresponds to formula I and X is oxygen,  $b$  is an integer from 0 to 2,  $R_2$  and  $R_3$  are independently  $C_1$ - $C_8$ alkyl,  $A$  is oxygen,  $y$  is 2 and  $R_4$  is hydrogen or a group of the formula Ib.

5. The composition of claim 4, wherein  $R_2$  and  $R_3$  are tert-butyl positioned ortho to the hydroxyl group and  $b$  is 2.

6. The composition of claim 1, wherein said hindered phenol corresponds to formula II.

7. The composition of claim 1, wherein said hindered phenol corresponds to formula II and  $R_2$  and  $R_3$  are independently  $C_1$ - $C_8$ alkyl,  $b$  is 2,  $d$  is 2 or 4 and  $Q_1$  is  $C_2$ - $C_{10}$ alkylene or pentaerythrityl.

8. The composition of claim 1, wherein said hindered phenol corresponds to formula III.

9. The composition of claim 1, wherein said hindered phenol corresponds to formula III and R<sub>2</sub> and R<sub>3</sub> are independently C<sub>1</sub>-C<sub>8</sub>alkyl, b is 2 and Q<sub>2</sub> is C<sub>2</sub>-C<sub>6</sub>alkylene.

10. The composition of claim 1, wherein said hindered phenol corresponds to formula IV.

11. The composition of claim 1, wherein said hindered phenol corresponds to formula IV and X and Y are oxygen, b is an integer from 0 to 2, R<sub>2</sub> and R<sub>3</sub> are independently C<sub>1</sub>-C<sub>8</sub>alkyl, z is 2, e is an integer from 3 to 20 and R<sub>6</sub> is a group of the formula Ia.

12. The composition of claim 11, wherein R<sub>2</sub> and R<sub>3</sub> are tert-butyl positioned ortho to the hydroxyl group.

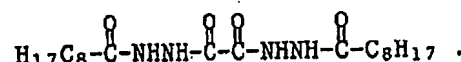
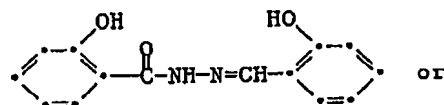
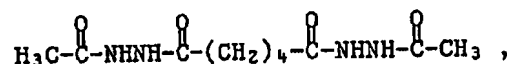
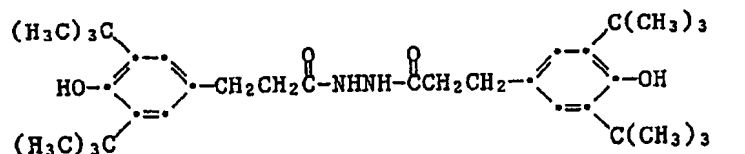
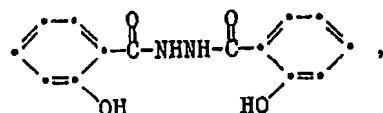
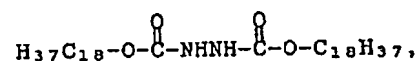
13. The composition of claim 1, wherein said hindered phenol is octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, 1,6-hexamethylene bis[3',5'-di-tert-butyl-4'-hydroxyhydrocinnamate], tetrakis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, N,N'-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamamide] or triethylene glycol bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

14. The composition of claim 1, wherein in component (b) R<sub>12</sub> and R<sub>13</sub> are independently C<sub>1</sub>-C<sub>18</sub>alkyl or a group of formula VIIIa, Z is a direct bond or C<sub>1</sub>-C<sub>6</sub>alkylene and the radicals R<sub>14</sub> are independently C<sub>4</sub>-C<sub>8</sub>alkyl, C<sub>5</sub>-C<sub>6</sub>cycloalkyl, phenyl or benzyl.

15. The composition of claim 14, wherein the OH in the group of the formula VIIIa and in the compounds of formula (X) is positioned either in the 2- or 4-position.

16. The composition of claim 15, wherein the OH in the group of the formula VIIIa is in the para-position, x is 2 and each R<sub>14</sub> is tert-butyl positioned ortho to the OH group.

17. The composition of claim 1, wherein said hydrazine is



18. The composition of claim 1, wherein said hindered phenol is 1,6-hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamate] and said hydrazine compound is N,N'-bis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine.

19. The composition of claim 1 comprising components (a) and (c).

20. The composition of claim 19, wherein component (c) is 2,2'-oxamido-bis[ethyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate].

21. The composition of claim 1 which additionally contains a basic co-stabilizer selected from the group consisting of calcium citrate, melamine, cyanoguanidine, polyamides, alkali and alkaline earth metal salts of fatty acids, amines, phosphites, phosphonites and peroxide-destroying compounds.

22. A method of stabilizing an acetal homo- or copolymer against thermal or oxidative degradation,

which comprises incorporating into said acetal components (a) and (b) or (a) and (c) according to claim 1.

23. A method of reducing color formation in acetal homo- or copolymers containing component (a) according to claim 1, which comprises incorporating into said acetal homo- or copolymers component (b) or (c) as defined in claim 1.

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